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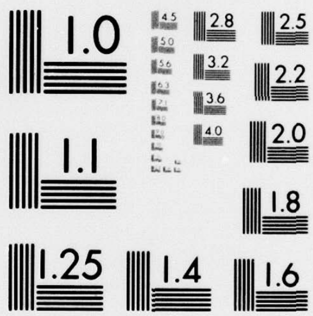
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ION-ION NEUTRALIZATION

by

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20. Abstract

The results of a preliminary study of the 3-body collision-stabilized neutralization reactions (i) $NO^+ + NO_2^- + He \rightarrow$ products and (ii) $SF_3^+ + SF_5^- + He \rightarrow$ products over the limited pressure range 1-8 torr in helium (the third body) are reported. The effective binary recombination coefficient, α_{eff}, is seen to increase with increasing pressure, from the pure binary value by a factor of about 2 for reaction (i) and by a factor of about 4 for reaction (ii). The need for measurements of α_{eff} for specific ion types but with differing third bodies (e.g. N_2, Ar) and as a function of temperature is discussed. This work is part of the wider programme of binary and ternary ionic recombination studies directed especially to those reactions thought to be important in the Earth's atmosphere.

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PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies, conducted by the authors of this report, which includes determinations of ion-molecule reaction rate coefficients and product ion distributions, electron-ion recombination coefficients and electron attachment coefficients. The work is largely intended as a contribution to the physics and chemistry of natural plasmas such as the Earth's atmosphere and the interstellar medium. A great deal of relevant data has been obtained principally because of our successful development and exploitation of the Langmuir probe/flowing afterglow and selected ion flow tube (SIFT) techniques. The work is largely supported by the Science Research Council.

CONTENTS

I INTRODUCTION

During the last few years we have developed a Langmuir Probe/ Flowing Afterglow technique with which we have been able to study a wide range of processes which occur in low temperature plasmas. The details of the technique and the scientific results of these studies have been given in previous reports and in several published papers (Smith et al 1975, Smith and Dean 1975, Smith and Church 1976, 1977, Smith et al 1976, Church and Smith, 1977, 1978, Smith et al 1978a, b). Our greatest effort has been made in the study of the binary mutual neutralization (ion-ion recombination) process and we have succeeded in determining binary ion-ion recombination coefficients, α_2, for many reactions of atmospheric interest, including those for reactions involving clustered positive ions (e. g. $H_3O^+(H_2O)_n$) and clustered negative ions (e. g. $NO_3^-.(HNO_3)_n$) (Smith et al 1978a, b). Additionally we have studied the temperature dependence of α_2 for two specific reactions over a limited temperature range appropriate to the atmosphere and have suggested the most suitable values of α_2 for use in mesospheric and stratospheric de-ionization rate calculations (Smith and Church 1977). We have also determined the neutral products of one reaction (i. e. $NO^+ + NO_2^-$) by observing the radiation emitted during the reaction (Smith et al 1978b).

D. Smith, N. G. Adams, A. G. Dean and M. J. Church, J. Phys. B. (1975), 8, 141

D. Smith and A. G. Dean, J. Phys. D., (1975), 8, 997

D. Smith and M. J. Church, Int. J. Mass Spectrom. Ion Phys., (1976), 19, 185

D. Smith and M. J. Church, Planet. Space Sci., (1977), 25, 433

D. Smith, N. G. Adams and M. J. Church., Planet. Space Sci., (1976), 24, 697

M. J. Church and D. Smith, Int. J. Mass Spectrom. Ion Phys., (1977), 23, 137

M. J. Church and D. Smith, J. Phys. D., (1978), 11, 2199

D. Smith, M. J. Church and T. M. Miller, J. Chem. Phys., (1978a), 68, 1224

D. Smith, N. G. Adams and M. J. Church, J. Phys. B., (1978b), 11, 4041

For the simple ions and relatively small cluster ions which we have studied to date, it is most probable that the mutual neutralization process results from an electronic transition near to a crossing of the potential energy surfaces of the ionic reactants and the neutral products. However, Bennett et al (1974) have suggested that the situation may be quite different if sufficient polar molecules are clustered to the core ions, in which case the ions would be more stable than the neutrals. Thus, mutual neutralization via transitions near potential surface crossing cannot occur, but rather the cluster ions would coalesce and the energy released would be utilized to "boil-off" clustered molecules. Alternatively, the ion-ion pair could retain its integrity as a "zwitterion". It is known that sufficiently large positive and negative ion clusters exist in the lower atmosphere and so it is important to attempt to determine the recombination coefficients for such ions and in doing so to answer the question "is the α_2 for such ions significantly different than for the smaller ionic species?" To obtain an answer by experiment, it is necessary to operate the flowing afterglow below room temperature at which clustering rates are sufficiently rapid and the larger cluster ions are stable against thermal decomposition. We are presently building a new flow tube which will be more readily operated at low temperatures than the existing one. Thus low temperature measurements are anticipated during the coming year.

Meanwhile we have turned our attention to the other major part of our overall programme of ionic recombination studies, that of 3-body (ternary) recombination. Previous studies of this process (Mahan, 1973) indicate that it will contribute significantly to the loss of ionization in the stratosphere and become dominant over the binary process below an altitude of about 30 kms (Smith and Church 1977). Thus, modern studies of this process are essential from the point of view of atmosphere deionization. Also a considerable interest in the fundamentals of the

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R. H. Bennett, D. L. Huestis, J. T. Moseley, D. Mukherjee, R. E. Olson, S. W. Benson, J. R. Peterson and F. T. Smith, A. F. C. R.L. Rept. AFCRL-TR-74-0417 (1974).

B. H. Mahan, Advances in Chem. Phys. (1973), 23, 1

D. Smith and M. J. Church, Planet. Space Sci. (1977), 25, 433

process exists (Flannery 1976, Bates and Mendas 1978). It is, of course, in the nature of the process that it must be studied at pressures sufficiently high that it begins to dominate over the binary process which is studied at low pressures ($\lesssim$ 1 torr). Our present technique is limited in its scope to pressures below about 10 torr in helium due to problems associated with the Langmuir probe technique. However, this is an important pressure range from the atmospheric viewpoint and insight into the process at these pressures will be of great value. Studies at higher pressures will require developments in our techniques.

We have, to date, made a preliminary study of two reactions over the approximate pressure range 1-8 torr in helium, viz:

$$NO^{+} + NO_2^{-} + He \rightarrow \text{products} \qquad (1)$$

and

$$SF_3^{+} + SF_5^{-} + He \rightarrow \text{products} \qquad (2)$$

Whilst reaction (2) has no atmospheric relevance its study should add to our understanding of the process, although our ultimate objective is to study cluster ions under high pressure conditions. However, the attainment of this objective will largely depend on our ability to create ion-ion plasmas in which these species are dominant.

II RESULTS

The details of the technique have been given previously. Briefly, ion-ion plasmas are created in a flow tube downstream of a microwave discharge which generates the ionization. Being remote from the ionization source, the plasma is thermalized and so the charged particle temperatures are characterised by the gas (vessel wall) temperature. The carrier gas (helium) pressure is sufficiently high to inhibit diffusive loss of ionization and the ionization density is made sufficiently high to ensure that its loss results from ionic recombination. Under these

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M. R. Flannery. "Ionic Recombination" in "Atomic Processes and Applications". North Holland Publ. Co. Amsterdam (1976) Chapter 12.

D. R. Bates and I. Mendas, Proc. Roy. Soc. Lond., (1978), A359, 275

conditions, the positive ion and/or negative ion density (n_+, n_-) is measured as a function of distance along the flow tube and is readily related to time by measuring the plasma flow velocity (Adams et al 1975). A reciprocal density versus time plot (i. e. n_+^{-1} or n_-^{-1} versus t) should then be linear, the slope of which provides the ionic recombination coefficient for the particular reaction under the prevailing conditions of pressure and temperature.

Fig. 1 shows such data obtained for reaction (1) at 300 K. Note the increasing slope of the plots with increasing helium pressure which represents an increasing coefficient for the neutralization reaction. This is a manifestation of the enhancement of the neutralization rate above that due to the binary mutual neutralization process alone. A similar situation results for reaction (2) as can be seen in the data given in Fig. 2, again obtained at 300 K. The reduced data, i. e. the effective binary rate coefficients, α_{eff}, as a function of helium pressure, are given in Table 1 and these are plotted in Fig. 3. Also given in Fig. 3 are our previously published data for the low pressure (pure binary) recombination coefficients for these reactions which are in excellent agreement with the present data.

As can be seen, no significant increase in α_{eff} occurs until the helium pressure in increased above about 2 torr. indicating the dominance of the pure binary process below these pressures. The increase with pressure above about 2 torr is clear and the two reactions respond to pressure increases very differently. The α_{eff} for the $NO^+ + NO_2^-$ reaction increases by a factor of about two over the available pressure range whereas that for the $SF_3^+ + SF_5^-$ reaction increases by a factor of greater than four over the same pressure range. Clearly, the factors which govern the pure binary process and lead to a value of α_2 for reaction (2) lower than for reaction (1) are being counteracted by the modest increase in helium pressure. This rapid increase in α_{eff} with pressure cannot, however, be maintained at the higher pressures, since

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N. G. Adams, M. J. Church and D. Smith, J. Phys. D. (1975), 8, 1409

there exists a good deal of evidence which suggests that α_{eff} increases to a maximum value of (2-4) x 10^{-6} $cm^3 s^{-1}$ at pressures of several hundreds of torr (Mahan 1973). Thus the rate of rise of α_{eff} with pressure must reduce. This preliminary data is very important, therefore, in one respect in that it does forcibly demonstrate that extrapolations of the high pressure data to obtain binary recombination coefficients, α_2, is invalid and, in fact, will lead to erroneously high values for α_2 even if other complications such as ionic clustering can be shown not to occur. The changing nature of the neutralization process is itself sufficient to render the extrapolation procedure invalid. This clearly explains why the α_2 deduced from extrapolated high pressure data (Mahan 1973) are consistently higher than the low pressure flowing afterglow data and thus gives even greater credence to our low pressure data. Further comment on these data and the next phase of this work are given in III below.

Also given in Table 1 are the measured values (as yet unpublished) of the binary recombination coefficients for three F^- reactions. The values obtained are consistent with all previous data for this process which at 300 K are within the range (4-10) x $10^{-8} cm^3 s^{-1}$ and were obtained as a prelude to further studies of the temperature dependence of α_2 for simple ion reactions.

III CONCLUSIONS

A start has been made on the study of the ternary ionic recombination process. The preliminary data have shown that α_{eff} increases rather rapidly with pressure in the range 2-8 torr in helium. Whilst the data is extremely interesting we have resisted drawing many conclusions from it since obviously more data is required and such is currently being obtained. No reliable theory is available describing α_{eff} in this transition region

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B. H. Mahan, Advances in Chem. Phys. (1973), 23, 1

between the pure binary regime and the collision enhanced (Thomson) regime, a region which is difficult to study theoretically. We expect that the experiment will probably lead the theory in this case.

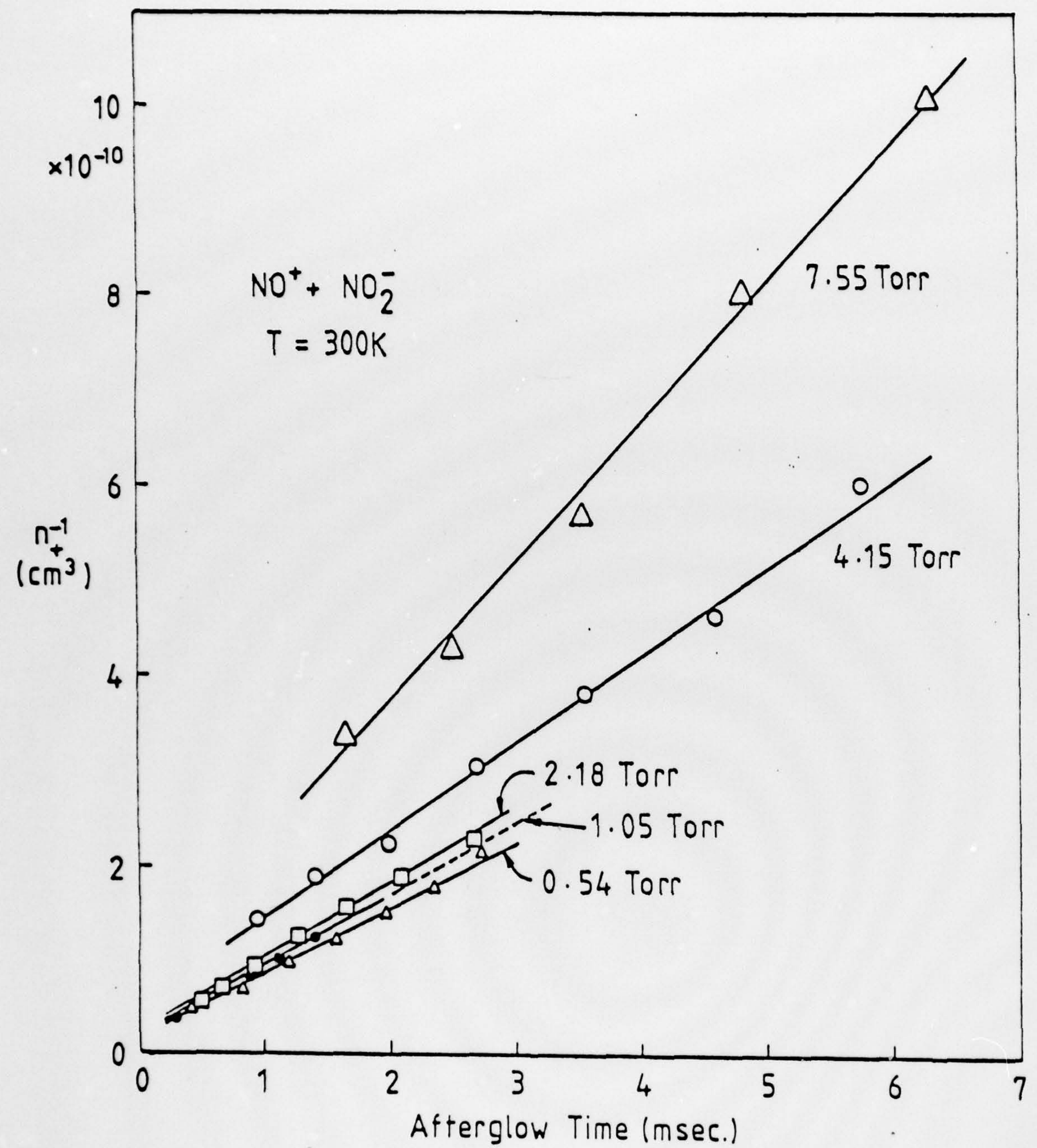
Our considered experimental approach to the problem of ternary recombination within the available pressure range is as follows:

(i) To obtain more detailed data for α_{eff} for the two reactions already studied and to study other reactions including cluster ion reactions at 300 K. using a helium carrier gas.

(ii) To investigate the temperature dependence of α_{eff} for selected reactions. The theory predicts (at least at higher pressures) that α_{eff} will have a rapid temperature dependence ($\sim T^{-3}$).

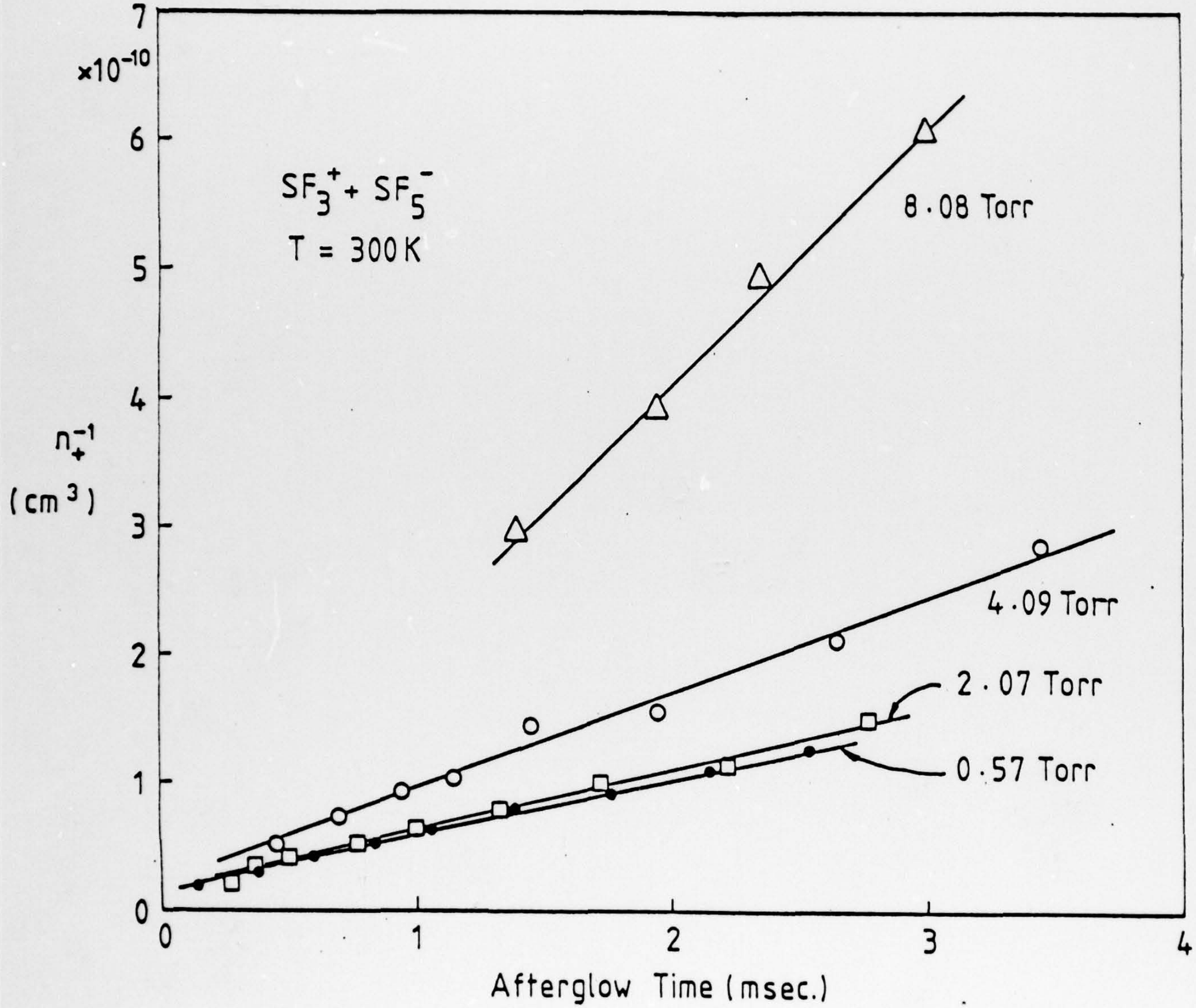
(iii) To investigate the influence on α_{eff} of the carrier gas type (the third body) by using argon and nitrogen as well as helium. It might be expected that the molecular gas N_2 will act as a more efficient third body i.e. that α_{eff} will increase more rapidly with increasing pressure at low pressures. The chemical reactivity of the N_2 may however limit these studies.

It is certain that these studies together with our continuing studies of the binary process will improve our understanding of the ionic recombination process and provide further data for use in atmospheric de-ionization rate calculations, including those for the higher pressure conditions in the lower atmosphere.



$NO^+ + NO_2^-$
T = 300K
7·55 Torr
4·15 Torr
2·18 Torr
1·05 Torr
0·54 Torr
n_+^{-1} (cm^3)
$\times 10^{-10}$
0
2
4
6
8
10
0
1
2
3
4
5
6
7
Afterglow Time (msec.)

FIGURE 1.



$SF_3^+ + SF_5^-$
T = 300 K
n_+^{-1} (cm^3)
$\times 10^{-10}$
0
1
2
3
4
5
6
7
8.08 Torr
4.09 Torr
2.07 Torr
0.57 Torr
Afterglow Time (msec.)

FIGURE 2.

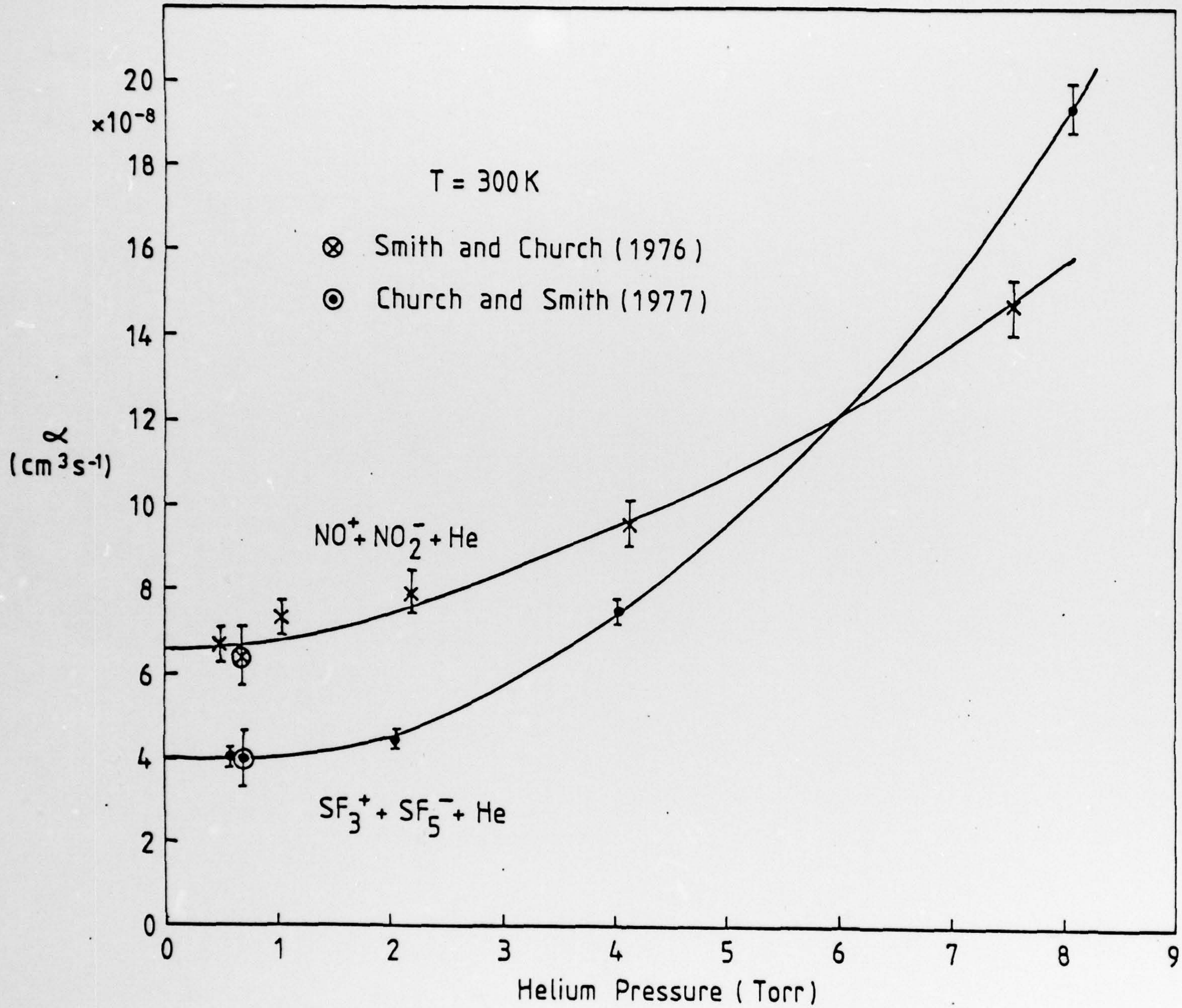

T = 300 K
⊗ Smith and Church (1976)
⊙ Church and Smith (1977)
$NO^+ + NO_2^- + He$
$SF_3^+ + SF_5^- + He$
α ($cm^3 s^{-1}$)
$\times 10^{-8}$
0
2
4
6
8
10
12
14
16
18
20
0
1
2
3
4
5
6
7
8
9
Helium Pressure (Torr)

FIGURE 3.

PRESENT IONIC RECOMBINATION DATA

Reaction	Pressure (Torr)	Effective Binary Recombination Coefficient ($cm^3 s^{-1}$)
$NO^+ + NO_2^- + He$	0.54	6.7(-8)
	1.05	7.3(-8)
	2.18	7.9(-8)
	4.15	9.6(-8)
	7.55	14.7(-8)
$SF_3^+ + SF_5^- + He$	0.57	4.1(-8)
	2.07	4.5(-8)
	4.09	7.5(-8)
	8.08	19.4(-8)
$CF_3^+ + F^-$	0.5	5.8(-8)
$NF_2^+ + F^-$	0.5	7.5(-8)
$N_2F^+ + F^-$	0.5	8.5(-8)

TABLE 1.

REFERENCES

D. Smith, N. G. Adams, A. G. Dean and M. J. Church, J. Phys. B. (1975), 8, 141

D. Smith and A. G. Dean, J. Phys. D., (1975), 8, 997

D. Smith and M. J. Church, Int. J. Mass Spectrom. Ion Phys., (1976), 19, 185

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D. Smith, N. G. Adams and M. J. Church., J. Phys. B., (1978b), 11, 4041

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M. R. Flannery. "Ionic Recombination" in "Atomic Processes and Applications". North Holland Publ. Co., Amsterdam (1976), Chapter 12.

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B. H. Mahan, Advances in Chem. Phys., (1973), 23, 1